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The structures of the isomorphous potassiun and rubidium salts of 4-nitrobenzoic acid and an overview of the features the metal complex stereochemistries of the alkali metal salt series with this ligand

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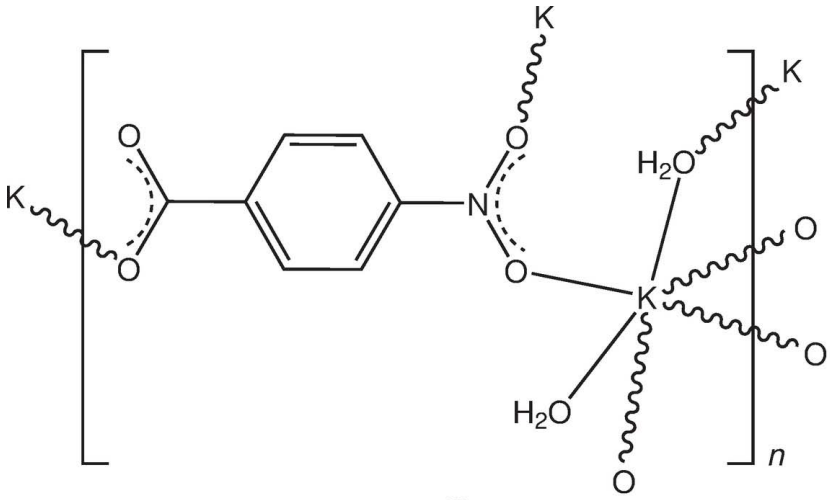
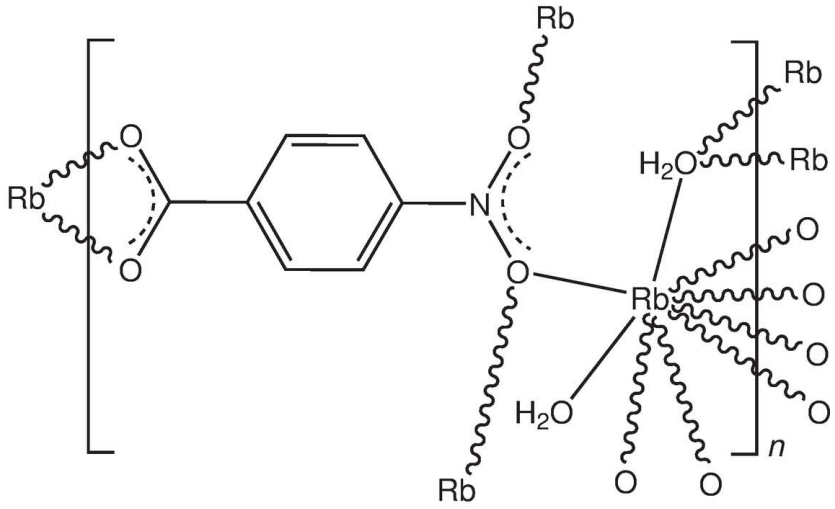
Abstract

The structures of the isomorphous potassium and rubidium polymeric coordination complexes with 4-nitrobenzoic acid, poly[μ-$_2$-aqua-aqua-μ-$_3$ (4-nitrobenzoato)-potassium], $[K(C_7H_4N_2O_2)(H_2O)_2]_n$, (I) and poly[$\mu$-$_3$-aqua-aqua-$\mu$-$_5$(4-nitrobenzoato)-rubidium], $[Rb(C_7H_4N_2O_2)(H_2O)_2]_n$, (II) have been determined. In (I) the very distorted KO_6 coordination sphere about the K^+ centres in the repeat unit comprise two bridging nitro O-atom donors, a single bridging carboxyl O-atom donor and two water molecules, one of which is bridging. In the the Rb complex (II), the same basic MO_6 coordination is found in the repeat unit but is expanded to RbO_9 through a slight increase in the accepted Rb—O bond length range and includes an additional Rb—$O_{carboxyl}$ bond, completing a bidentate O,O′</i-chelate interaction, and additional bridging Rb—O_{nitro} and Rb—O_{water} bonds. The comparative K—O and Rb—O bond length ranges are 2.738 (3)–3.002 (3) Å (I) and 2.884 (2)–3.182 (2) Å (II). The structure of (II) is also isomorphous as well as isostructural with the known structure of the nine-coordinate caesium 4-nitrobenzoate analogue, $[Cs(C_7H_4N_2O_2)(H_2O)_2]_n$, (III) in which the Cs—O range is 3.047 (4)–3.338 (4) Å. In all three complexes, common basic polymeric extensions are found, including two different centrosymmetric bridging interactions through both water and nitro groups as well as extensions along c through the p-related carboxyl group, giving a two-dimensional structure in (I). In (II) and (III), three-dimensional structures are generated through additional bridges the nitro and water O-atoms. In all structures, both water molecules are involved in similar intra-polymer O—H···O hydrogen-bonding interactions to both carboxyl as well as water O-atom acceptors. A comparison of the varied coordination behaviour of the full set of Li–Cs salts with 4-nitrobenzoic acid is also made.



(I)



(II)

1. Comment

4-Nitrobenzoic acid (PNBA) has proved to be a useful ligand for the preparation of metal complexes, which are mainly monomeric but rarely involve the nitro group in coordination. The known structures of the alkali metal salts of PNBA are a lithium salt (a trihydrate) (Srinivasan et al., 2012), a sodium salt (a trihydrate) (Turowska-Tyrk et al., 1988), an anhydrous potassium salt (a 1:1 salt-acid adduct) (Shrivastava & Speakman, 1961) and a caesium salt (a dihydrate) (Smith, 2013a). However, the structure of the rubidium salt had not been reported. In an attempt to complete the structures of this series of compounds, reaction of 4-nitrobenzoic acid with Rb_2CO_3 in aqueous ethanol afforded good crystals of the Rb complex while a parallel reaction with K_2CO_3, provided the hydrated K salt. The structures of these two salts, $[K(C_7H_4NO_2)(H_2O)_2]_n$, (I) and $[Rb(C_7H_4NO_2)(H_2O)_2]_n$, (II) are reported herein.

The previously reported K complex polymeric adduct $[K(PNBA)\cdots H—(PNBA)]_n$ (Srivastava & Speakmam, 1961) was an early example of a Type B complex having the anionic and adduct ligand species coordinated, with the two linked by a very short carboxyl O—H···O hydrogen bond (2.49 Å). This example is different from the Type A complex found in the rubidium complex with 2-nitrobenzoic acid (ONBA), $[Rb(ONBA\cdots H\cdots ONBA)]_n$ (Shrivastava & Speakman, 1961), in

which the ligand species [hydrogen bis(ONBAH)] has the acid H-atom delocalized on a crystallographic inversion centre within a typically short hydrogen bond (O···O, 2.43 Å). This Type A species was earlier described in the potassium hydrogen bis(phenylacetate) structure (Speakman, 1949) and a little later in the potassium hydrogen bis(aspirinate) structure (Manojlović & Speakman, 1967; Sequeira et al., 1968) and in the rubidium hydrogen bis(aspirinate) analogue (Grimvall & Wengelin, 1967).

The simple formulae for the alkali metal salts of PNBA (dihydrates, trihydrates) give no indication of the actual coordination features for the metals involved in the common polymeric structures described in this series. A short review of the metal stereochemical features of the complete series of alkali metal complexes with PNBA (Li, Na, Cs) is also provided here to illustrate the complex diversity.

In the structures of the title K and Rb complexes with PNBA [(I) and (II), respectively], the crystals have been confirmed as being isomorphous on the basis of cell parameters, space group, and cell contents (Table 1) and confirmed by the successful phasing and refining of the structure of (II) using the full set of heavy atom atomic coordinates from (I). However, the extension to isostructurality is upset by the consideration of the acceptable K—O and Rb—O bond length maxima for these structures, altering the coordination number, which in the structure of (I) is six and in (II), nine. This expansion is primarily through an asymmetric bidentate O,O′-chelate (Rb) vs monodentate carboxyl O-interaction (K) and additional nitro-O and water-O bridges. Both coordination polymeric structures are based on common MO_6 complex units and will be described concurrently where possible.

With the K structure (I), the very distorted KO_6 coordination sphere (Fig. 1) comprises two bridging nitro O-atom donors (O42, O41^{i}), a single bridging carboxyl O-atom donor (O11^{ii}), a bridging water molecule (O2W, O2W^{i}) and a monodentate water (O1W) (for symmetry codes, see Table 2). The K—O bond range is 2.7352 (14)–3.0051 (14) Å, comparing with 2.70 (1)–2.82 (1) Å for the [K(PNBA)-H-(PNBA)]$_n$ structure (Shrivastava & Speakman, 1961). Two types of centrosymmetric cyclic, water-nitro group quadruple bridges link the K centres, one 8-membered through a water and two O-atoms of a bridging nitro group (O41, O42), the second 6-membered through a water and a single nitro O-atom (O42) (Fig. 2). The K1···K1^{i} and K1···K1^{viii} separations are 4.2177 (6) and 3.9819 (6) Å, respectively [for symmetry code (viii): -x +2, -y +1, -z +2]. Further structure extension is through the p-related carboxyl substituent group of the anti-parallel PNBA ligands linking the K centres across c and down b, giving an overall two-dimensional coordination polymer.

With the Rb complex (II), the same bonding interactions as described for the KO_6 coordination sphere in (I) are present. However, the expansion of the coordination sphere to RbO_9 (Table 3, Fig. 3) from the KO_6 sphere, as mentioned previously, i.e. two bridging nitro O-atom donors, (O42, O41^{i}), a single bridging carboxyl O-atom donor (O11^{iii}), a bridging water molecule (O2W^{i}) and a monodentate water molecule (O1W), results from three additional Rb—O bonds (Table 3) (Fig. 3). The Rb—O bond range is 2.884 (3)–3.182 (2) Å. The additional bonds in (II) are: a, to the second carboxyl-O atom (O12^{ii}), completing a bidentate O,O′)-chelate interaction [the equivalent K1—O12^{ii} distance in (I) is 3.155 (3) Å]; b, to the second nitro O-atom (O42^{ii}), forming also a bridge [comparative distance in (I), 3.110 (3) Å]; c, a third bridging link to O2W^{ii} [comparative distance in (I), 3.132 (2) Å]. The two Rb···Rb separations within the centrosymmetric cyclic bridges described for (I) are 4.3584 (7) and 4.1152 (7) Å, respectively (Fig. 4). Structure extension through the p-related carboxyl substituent group of the PNBA ligand such as found in (I) is also present in (II) giving a three-dimensional polymer.

The crystal structures of (I) and (II) are stabilized by similar intra-polymer water O—H···$O_{carboxyl}$ and O—H···O_{water} hydrogen-bonding interactions (Tables 4, 5). The comparative crystal packing for (I) and (II) are shown in Fig. 5 and Fig. 6, respectively. No inter-ring π–π interactions are present in either structure, with minimun ring centroid separations of 4.5362 (17) Å (I) and 4.5991 (19) Å (II).

The structure of the dihydrate Cs salt of PNBA $[Cs(PNBA)(H_2O)_2]_n$, (III) (Smith, 2013a) is both isomorphous and isostructural with that for the Rb complex (II). However, the Cs structure was originally described in terms of the $P2_1/n$ unit cell which transforms to the $P2_1/c$</> variant as in (I) and (II) with comparative unit cell parameters of a = 6.0700 (3), b = 7.1073 (4), c = 24.5500 (13) Å, β = 100.240 (5)°, V. = 1024.2 (1) Å^3. The Cs—O bond length range in the CsO_9 coordination sphere is 3.047 (4)–3.338 (4) Å (Fig. 7) and the Cs···Cs separations within the common centrosymmetric dimer repeat units are 4.4583 (4) and 4.2610 (4) Å, respectively. The hydrogen-bonding in the three-dimensional structure is also identical to that found in (II). It is of interest that the ammonium salt of PNBA (Smith, 2014b), the two-dimensional hydrogen-bonded $[NH_4^+(PNBA)^-(H_2O)_2]$ polymer, may also be considered isomorphous with (I)–(III), having the cell parameters a = 5.948 (4), b = 6.9049 (5), c = 24.2780 (15) Å, β = 100.740 (6)°, V. = 987.34 (12) Å^3, space group $P2_1/c$</>.

The type of structure extension through the para-related nitro and carboxyl substituent groups of the PNBA ligand as found in (I), (II) and (III) is similar to those found in the alkali metal salts of 4-nitroanthranilic acid: sodium (a dihydrate) and potassium (a monohydrate) (Smith, 2013b), rubidium (a monohydrate) (Smith, 2014b) and caesium (a monohydrate) (Smith & Wermuth, 2011).

The comparative features of the metal coordination found in the other known 4-nitrobenzoates of the alkali metal series (Li–K) are provided below for general interest. For easier comparison, the atom naming naming for the PNBA ligands in each has been altered to be consistent with that used in the present structures (I) and (II) and with the Cs structure (III) (Smith, 2013a). These structures are: with Li, (IV) (Shrinivasan et al., 2012); with Na, (V) (Turowska-Tyrk et al., 1988 and with K, (VI) (Srivastava & Speakman, 1967).

(1) The lithium compound with PNBA, described simply as Li^+ $(PNBA)^-$. $3H_2O$ is, in the solid state, is a true 'salt′, $[Li_2(H_2O)_6)]^+$ $2(PNBA)^-$, (IV) (Srinivasan et al., 2012) with no coordinative linkage between the cation and the two $PNBA^-$ anions. The unusual centrosymmetric cation cage is dimeric with the two tetrahedral LiO_4 centres comprising two bridging water O-donors and two monodentate water donors. Extensive O—H···O hydrogen-bonding interactions give a three-dimensional network structure involving the water molecules and carboxyl, nitro and water O-atom acceptors (Fig. 8).

(2) The sodium compound with PNBA is also simply described as $Na^+(PNBA)^-$. $3(H_2O)$ but is in fact a one-dimensional coordination polymer based on $[Na_2(PNBA)(H_2O)_6]^+$ cation units with $(PNBA)^-$ counter anions (V) (Fig. 9) (Turowska-Tyrk et al., 1988). The two independent Na^+ complex centres are different, and are multiply bridged by five water molecules and a nitro group of the coordinating PNBA ligand in a bidentate O,O′ mode, with two of the water molecules monodentate. The two anionic PNBA species are strongly π–associated [minimum ring centroid separation = 3.5433 (13) Å], while extensive water O—H···O hydrogen-bonding associations to both carboxyl, nitro and water O-atom acceptors give an overall three-dimensional structure.

(3) The previously mentioned Type A potassium adduct compound with PNBA, simply described as K^+ $(PNBA^-)$.(PNBA) (potassium hydrogen bis(4-nitrobenzoate) is a coordination polymer, $[K(PNBA)\text{-}H\text{-}(PNBA)]_n$, (VI) (Shrivastava & Speakman, 1961). The stereochemistry of the KO_6 complex repeat unit is described as distorted octahedral having both anionic and adduct molecules linked through a short H-bond and coordinated through five separate carboxyl O-atoms and a nitro O-atom donor (Fig. 10). Polymeric extensions generate a two-dimensional sheet structure in which no π–π interactions are present.

The PNBA species within the overall set of alkali metal complexes are essentially planar: the torsion angles defining the rotation of the carboxyl and nitro groups out of the benzene plane (C2—C1—C11—O11 and C3—C4—N4—O42, respectively) being 169.4 (3) and 179.4 (3)° in (I) and 173.8 (4) and 177.2 (3)° in (II), comparing with maximum deviations from the plane [160.2 (2)° (carboxyl) in the uncoordinated PNBA anion of the Na complex (V) and 166.6 (2)°

(nitro) in the coordinated PNBA ligand in the same Na complex] ((Turowska-Tyrk et al., 1988]. This 'planar' conformation is also found in the monoclinic polymorphs of the parent acid [Tavale & Pant, 1971; Tonogaki et al., 1993 (C2/c) and Groth, 1980; Bolte, 2009 ($P2_1/c$)].

2. Synthesis and crystallization

The title K and Rb complexes (I) and (II) were synthesized by heating together for 5 minutes, 0.5 mmol (167 mg) of 4-nitrobenzoic acid and either excess K_2CO_3 or Rb_2CO_3 in 15 ml of 10% ethanol–water. Partial room temperature evaporation of the solutions gave in both cases, colourless elongated crystal plates of the title compounds from which specimens were cleaved for the X-ray analyses.

3. Refinement

The experimental details for compounds (I) and (II) are listed in Table 1. Carbon-bound hydrogen atoms were placed in calculated positions [C—H = 0.95 Å] and allowed to ride in the refinement, with $U_{iso}(H) = 1.2U_{eq}(C)$. Hydrogen atoms of the coordinated water molecule were located in difference-Fourier syntheses but were subsequently allowed to ride, with $U_{iso}(H) = 1.5U_{eq}(O)$. Minor twinning was identified in the crystal of (I) [*PLATON* (Spek, 2009)] (law -1 0 - 0.003, 0 - 1 0, 1 0 1), giving a refined BASF factor of 0.02725).

fig1.tif

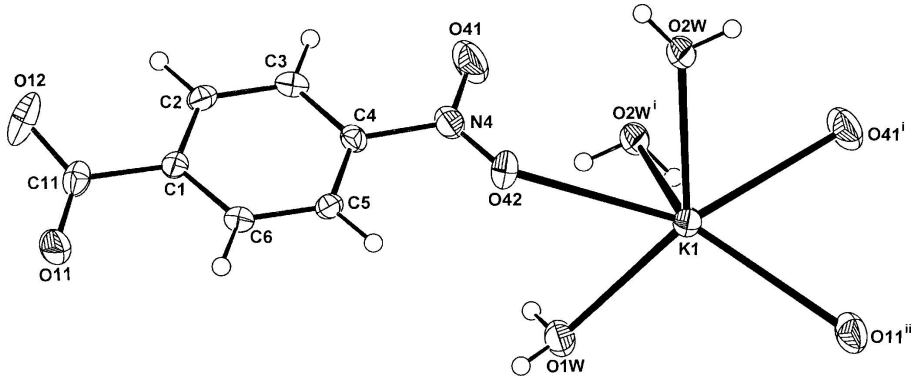


Figure 1

The molecular configuration and atom-numbering scheme for the coordination polyhedron of complex (I), with non-H atoms drawn as 40% probability displacement ellipsoids. For symmetry codes: see Table 2.

fig2.tif

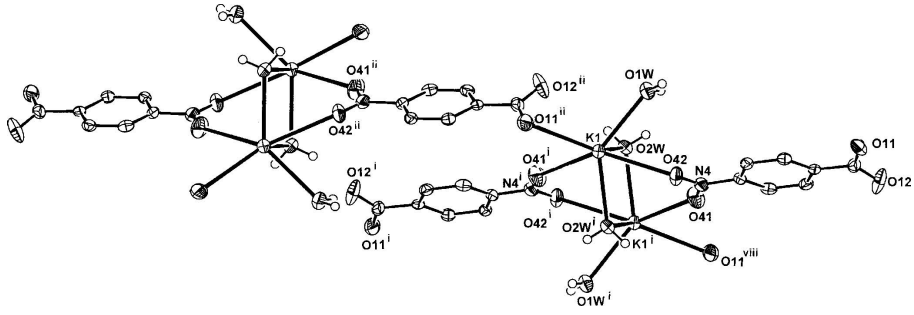


Figure 2

A partial expansion of the KO_6 coordination sphere in the polymeric structure of (I). For symmetry code (viii): $-x + 1$, $y - 1/2$, $-z + 3/2$. For other symmetry codes see Fig. 1 and Table 2.

fig3.tif

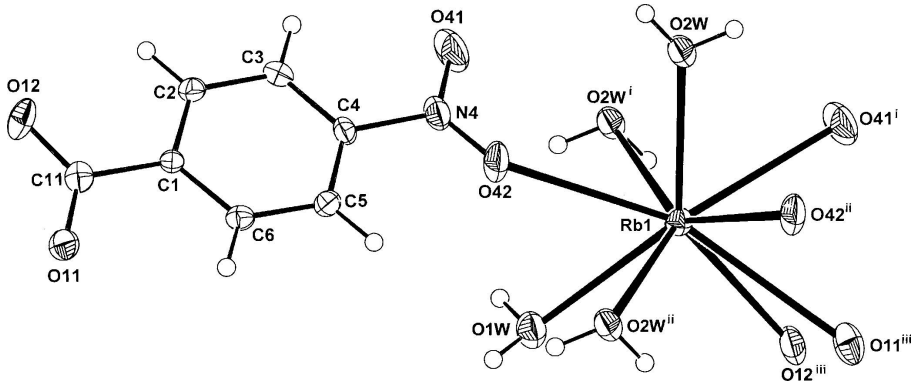


Figure 3

The molecular configuration and atom-numbering scheme for the coordination polyhedron of complex (II), with non-H atoms drawn as 40% probability displacement ellipsoids. For symmetry codes: see Table 3.

fig4.tif

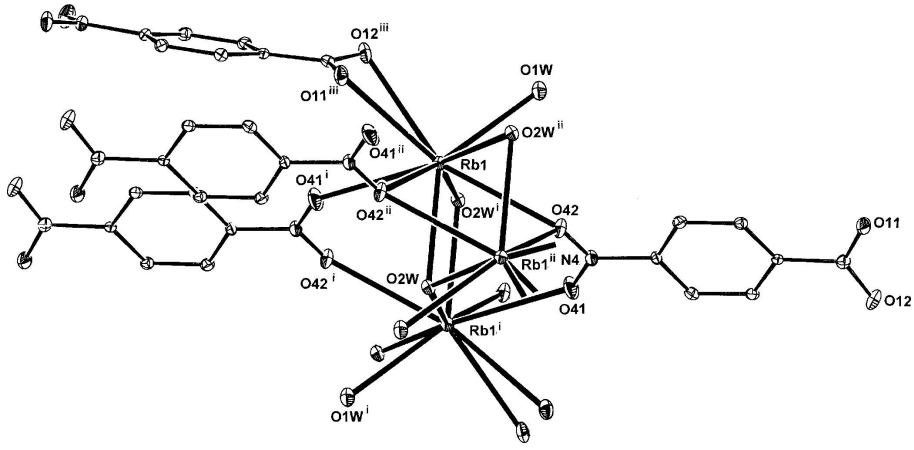


Figure 4

A partial expansion of the RbO_9 coordination sphere in the polymeric structure of (II). For symmetry codes codes, see Fig. 2 and Table 3.

fig5.tif

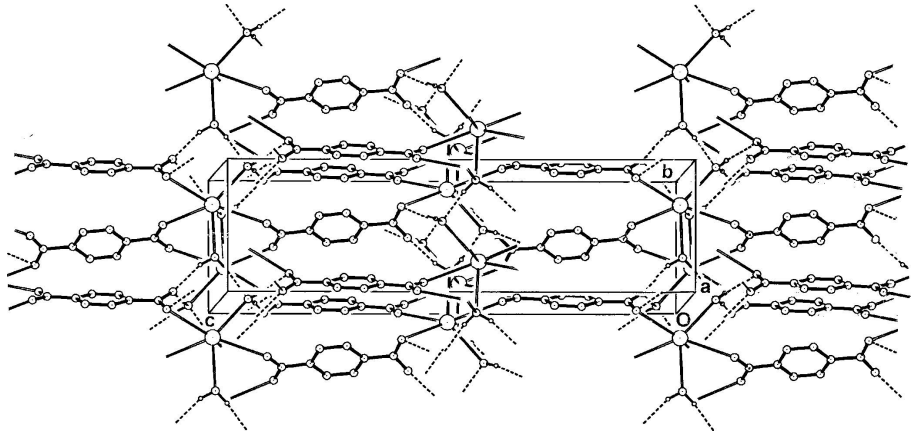


Figure 5

The packing of the hydrogen-bonded structure of (I) in the unit cell viewed down *a*. Hydrogen-bonding associations are shown as dashed lines.

fig6.tif

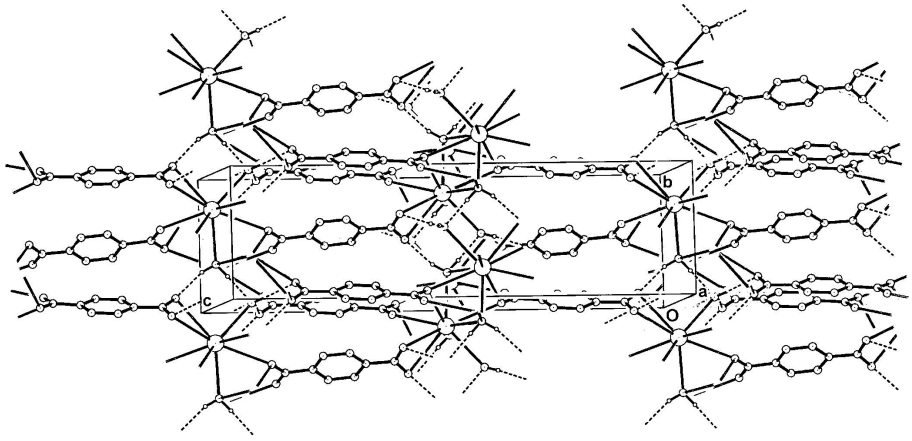


Figure 6

The packing of the hydrogen-bonded structure of (II) in the unit cell viewed down *a*. Hydrogen-bonding associations are shown as dashed lines.

fig7.tif

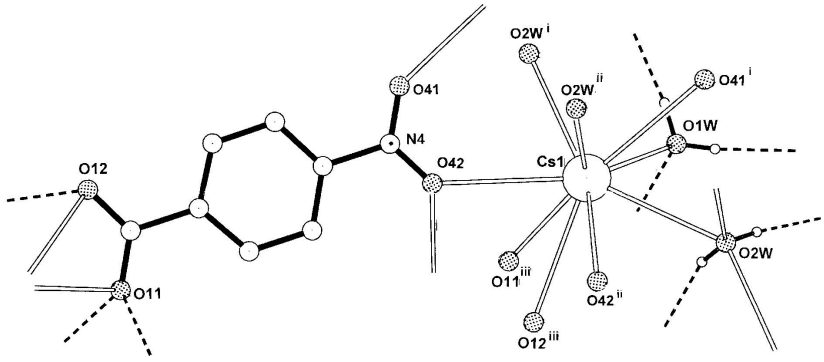


Figure 7

The coordination sphere, polymeric and hydrogen-bond extensions in the $[Cs(PNBA)(H_2O)_2]_n$ structure, (III) (Smith, 2013*a*). For symmetry codes: (i) -*x* + 1, -*y* + 1, -*z* + 2; (ii) -*x* + 2, -*y* + 1, -*z* + 2; (iii) *x*, -*y* + 3/2, *z* + 1/2. + 1

fig8.tif

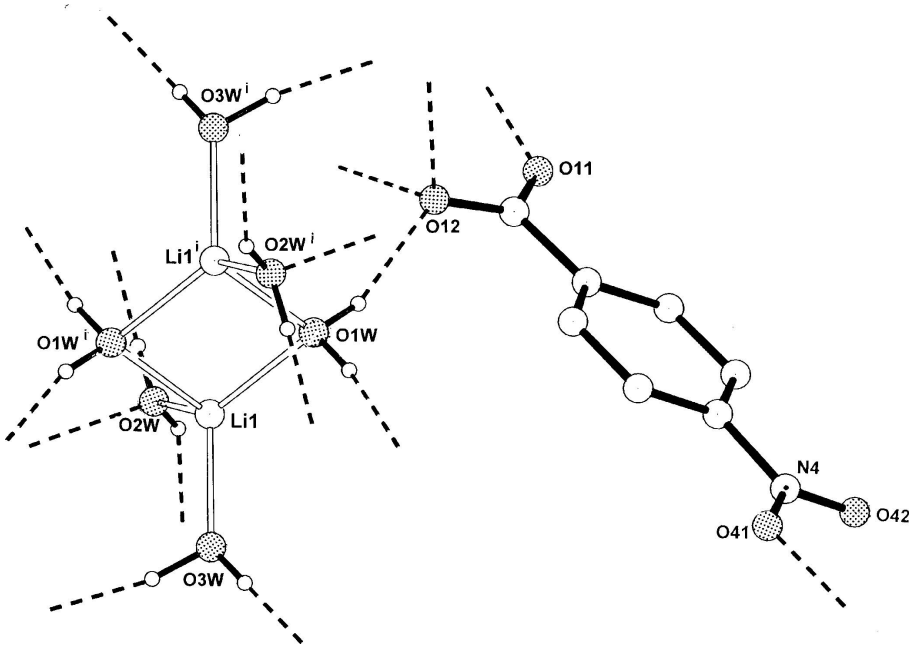


Figure 8

The Li^+ coordination and hydrogen-bond extensions in the $[Li_2(H_2O)_6)]^+$ 2(PNBA)$^-$ structure, (IV) (Srinivasan *et al.*, 2012). The second inversion-related PNBA anion is not shown. For symmetry codes: (i) -*x*, -*y* + 1, -*z* + 1.

fig9.tif

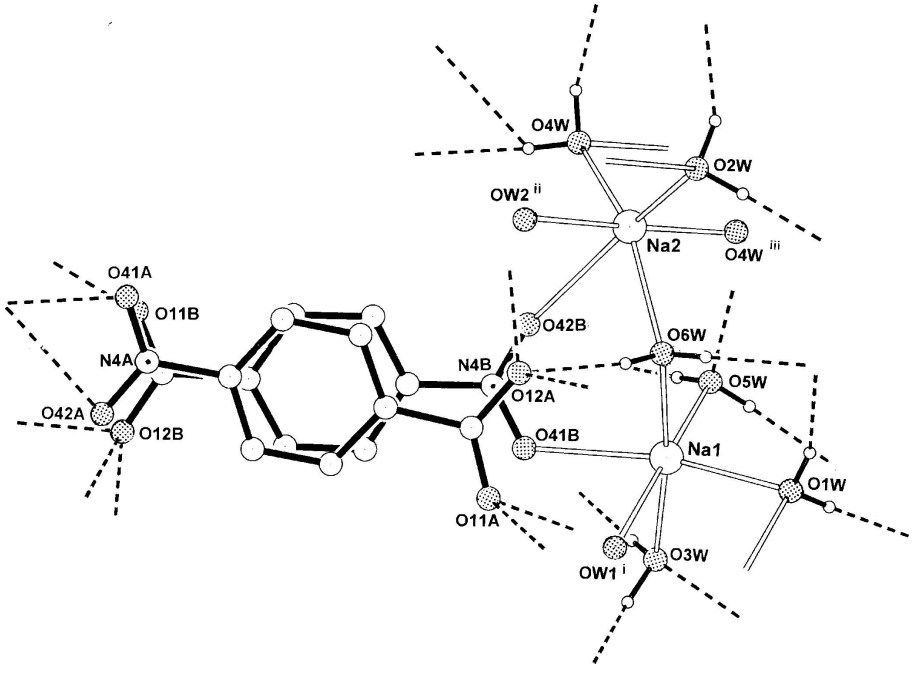


Figure 9

The coordination sphere, polymeric and hydrogen-bond extensions in the $[Na_2(H_2O)_6(PNBA)^+]_n$. *n*(PABA$^-$) structure, (V) (Turowska-Tyrk *et al.*, 1988). For symmetry codes: (i) -*x*, -*y*, -*z* + 1; (ii) -*x*, -*y* + 1, -*z* + 2; (iii) -*x* + 1, -*y* + 1, -*z* + 2.

fig10.tif

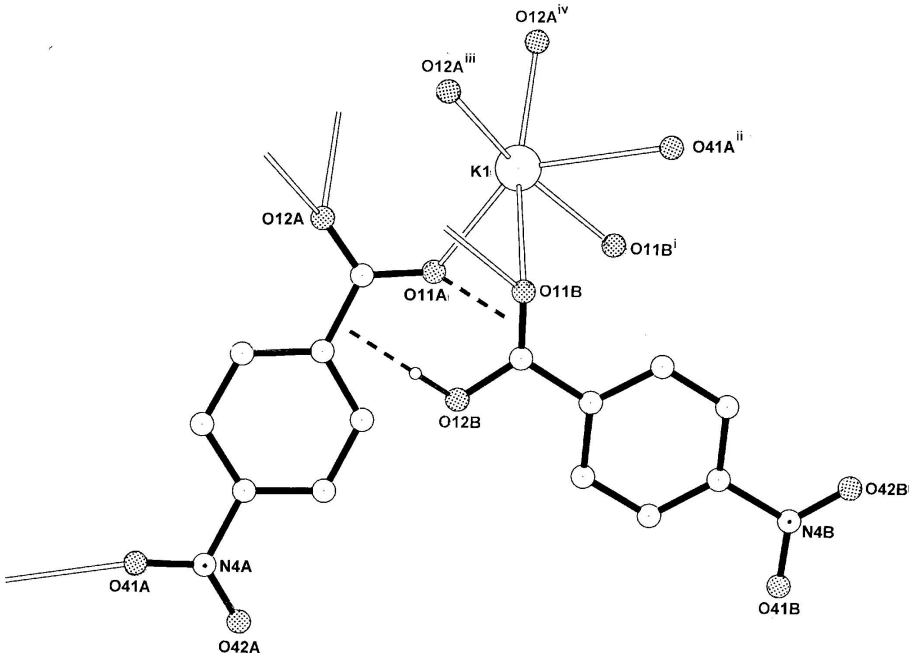


Figure 10

The coordination sphere, polymeric and hydrogen-bond extensions in the [K(PNBA)-H-(PNBA)]$_n$ structure, (VI) (Srivastava & Speakman, 1961). For symmetry codes: (i) *x*, *y* + 1, *z*; (ii) *x, y + 1, z + 1; (iii) -x, -y, -z; (iv) -x, -y + 1, -z.*

Table 1

Experimental details

	(I)	(II)
Crystal data		
Chemical formula	$C_7H_8KNO_6$	$C_7H_8NO_6Rb$
M_r	241.24	287.61
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	200	200
a, *b*, *c* (Å)	5.8217 (4), 6.9692 (5), 23.8602 (16)	5.9355 (5), 7.0456 (7), 24.204 (2)
β (°)	97.299 (6)	98.739 (8)
V (Å^3)	960.23 (12)	1000.44 (16)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.56	4.96
Crystal size (mm)	0.30 × 0.25 × 0.08	0.31 × 0.24 × 0.10
Data collection		
Diffractometer	Oxford Diffraction Gemini-S CCD-detector diffractometer	Oxford Diffraction Gemini-S CCD-detector diffractometer
Absorption correction	Multi-scan *CrysAlis PRO* (Agilent, 2013)	Multi-scan *CrysAlis PRO* (Agilent, 2013)
T_{min}, T_{max}	0.945, 0.980	0.549, 0.980

No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3638, 1886, 1755	3439, 1969, 1692
R_{int}	0.019	0.032
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617	0.617
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.073, 1.04	0.034, 0.082, 0.97
No. of reflections	1886	1969
No. of parameters	136	137
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.22	0.51, −0.51

Computer programs: *CrysAlis PRO* (Agilent, 2013), *CrysAlis PRO*, *SHELXS97* (Sheldrick, 2008), *SIR92* (Altomare *et al.*, 1993), *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012), *PLATON* (Spek, 2009), *PLATON* (Spek, 2008), *PLATON*.

Table 2

Selected bond lengths (Å) for (I)

K1—O1W	2.7816 (14)	K1—O2W^{i}	3.0029 (12)
K1—O2W	2.7352 (14)	K1—O41^{i}	2.9752 (17)
K1—O42	2.9681 (15)	K1—O11^{ii}	3.0051 (14)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) *x*, −*y*+3/2, *z*+1/2.

Table 3

Hydrogen-bond geometry (Å, º) for (I)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H11W···O12^{iii}	0.87	1.84	2.6994 (17)	170
O1W—H12W···O11^{iv}	0.85	1.88	2.7101 (19)	165
O2W—H21W···O12^{v}	0.85	1.96	2.785 (2)	162
O2W—H22W···O1W^{vi}	0.87	1.90	2.7534 (18)	170

Symmetry codes: (iii) −*x*+1, *y*+1/2, −*z*+3/2; (iv) −*x*+2, *y*+1/2, −*z*+3/2; (v) *x*, −*y*+1/2, *z*+1/2; (vi) *x*, *y*−1, *z*.

Table 4

Selected bond lengths (Å) for (II)

Rb1—O1W	2.938 (3)	Rb1—O2W^{ii}	3.182 (2)
Rb1—O2W	2.884 (2)	Rb1—O42^{ii}	3.165 (3)
Rb1—O42	3.119 (3)	Rb1—O11^{iii}	3.165 (3)
Rb1—O2W^{i}	3.105 (2)	Rb1—O12^{iii}	3.155 (3)
Rb1—O41^{i}	3.112 (3)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) −*x*+2, −*y*+1, −*z*+2; (iii) *x*, −*y*+3/2, *z*+1/2.

Table 5

Hydrogen-bond geometry (Å, º) for (II)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H11W···O12^{iv}	0.93	1.80	2.720 (3)	169
O1W—H12W···O11^{v}	0.82	1.89	2.706 (4)	174
O2W—H21W···O12^{vi}	0.86	1.95	2.790 (4)	163
O2W—H22W···O1W^{vii}	0.87	1.88	2.752 (4)	176

Symmetry codes: (iv) $-x+1, y+1/2, -z+3/2$; (v) $-x+2, y+1/2, -z+3/2$; (vi) $x, -y+1/2, z+1/2$; (vii) $x, y-1, z$.

Acknowledgements

The authors acknowledge financial support from the Science and Engineering Faculty, Queensland University of Technology.

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checkCIF/PLATON results for paper t099772

checkCIF/PLATON results
Ellipsoid plot

checkCIF/PLATON results

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: C-C = 0.0021 A Wavelength=0.71073
Cell: a=5.8217(4) b=6.9692(5) c=23.8602(16)
alpha=90 beta=97.299(6) gamma=90
Temperature: 200 K

	Calculated	Reported
Volume	960.23(12)	960.23(12)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C7 H8 K N O6	C7 H8 K N O6
Sum formula	C7 H8 K N O6	C7 H8 K N O6
Mr	241.24	241.24
Dx,g cm-3	1.669	1.669
Z	4	4
Mu (mm-1)	0.562	0.562
F000	496.0	496.0
F000'	497.11	
h,k,lmax	7,8,29	7,8,29
Nref	1889	1886
Tmin,Tmax	0.845,0.956	0.945,0.980
Tmin'	0.845	

Correction method= # Reported T Limits: Tmin=0.945 Tmax=0.980 AbsCorr = MULTI-SCAN
Data completeness= 0.998
Theta(max)= 26.000
R(reflections)= 0.0299(1755) wR2(reflections)= 0.0734(1886)
S = 1.042 Npar= 136

Alert level C

PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for ..... O42 Check

Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension 2 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 4 Report
PLAT128_ALERT_4_G Alternate Setting for Input Space Group P21/c P21/n Note
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed .. ! Info
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Th(Min) ... 2 Report
PLAT931_ALERT_5_G Found Twin Law ( )[1 0 2] Estimated BASF 0.03 Check

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

1 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
3 ALERT type 5 Informative message, check

Datablock: II

Bond precision: C-C = 0.0046 A Wavelength=0.71073
Cell: a=5.9355(5) b=7.0456(7) c=24.204(2)
alpha=90 beta=98.739(8) gamma=90
Temperature: 200 K

	Calculated	Reported
Volume	1000.44(16)	1000.44(16)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C7 H8 N O6 Rb	C7 H8 N O6 Rb
Sum formula	C7 H8 N O6 Rb	C7 H8 N O6 Rb
Mr	287.61	287.61
Dx,g cm-3	1.910	1.910
Z	4	4
Mu (mm-1)	4.958	4.958
F000	568.0	568.0
F000'	564.60	
h,k,lmax	7,8,29	7,8,29
Nref	1973	1969
Tmin,Tmax	0.249,0.609	0.549,0.980
Tmin'	0.207	

Correction method= # Reported T Limits: Tmin=0.549 Tmax=0.980 AbsCorr = MULTI-SCAN
Data completeness= 0.998
Theta(max)= 26.000
R(reflections)= 0.0340(1692) wR2(reflections)= 0.0823(1969)
S = 0.966 Npar= 137

Alert level C

PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 2.208 Check
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 2 Report

---

Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension 3 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 4 Report
PLAT128_ALERT_4_G Alternate Setting for Input Space Group P21/c P21/n Note
PLAT899_ALERT_4_G SHELXL97 is Deprecated and Succeeded by SHELXL 2014 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Th(Min) ... 2 Report

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

---

database duplication summary

Datablock: I

- **Chemical name = potassium 4-nitrobenzoate dihydrate**
- *R* factor = 0.030
- Space group = P 21/c
- Formula = C7 H8 K N O6
- a=5.8217 b=6.9692 c=23.8602
- alpha=90 beta=97.299 gamma=90

Datablock: II

- **Chemical name = rubidium 4-nitrobenzoate dihydrate**
- *R* factor = 0.034
- Space group = P 21/c
- Formula = C7 H8 N O6 Rb
- a=5.9355 b=7.0456 c=24.204
- alpha=90 beta=98.739 gamma=90

No duplication found.

reference checking results

The following references were not checked in detail as they were not recognized as journal references

Agilent (2013). *CrysAlis PRO*. Agilent Technologies Ltd., Yarnton, Oxfordshire, England.

Bolte, M. (2009). Private communication (refcode NBZOAC011). CCDC, Cambridge, England.

The following reference may be incorrectly formatted

Srinivasan, B. R., Shetgaonkar, S. Y., Dhavskar, K. T., Sundar, J. K. & Natarajan, S. (2012). *Ind. J. Chem. A* **51**, 564--570.
[*Unrecognized journal title.*]

Results of online verification of references to IUCr journals

No result for Spek, A. L. (2009). *Acta Cryst.* D**65**, 144--152.
(searched using volume and page)

No result for Tavale, S. S. & Pant, L. M. (1971). *Acta Cryst.* **27**, 1471--1481.
(searched using volume and page)

The following references do not appear to be cited

Smith, G. & Wermuth, U. D. (2013). *Acta Cryst.* C**69**, 1472--1477.

Smith, G. (2014*a*). *Acta Cryst.* C**70**, 315--319.

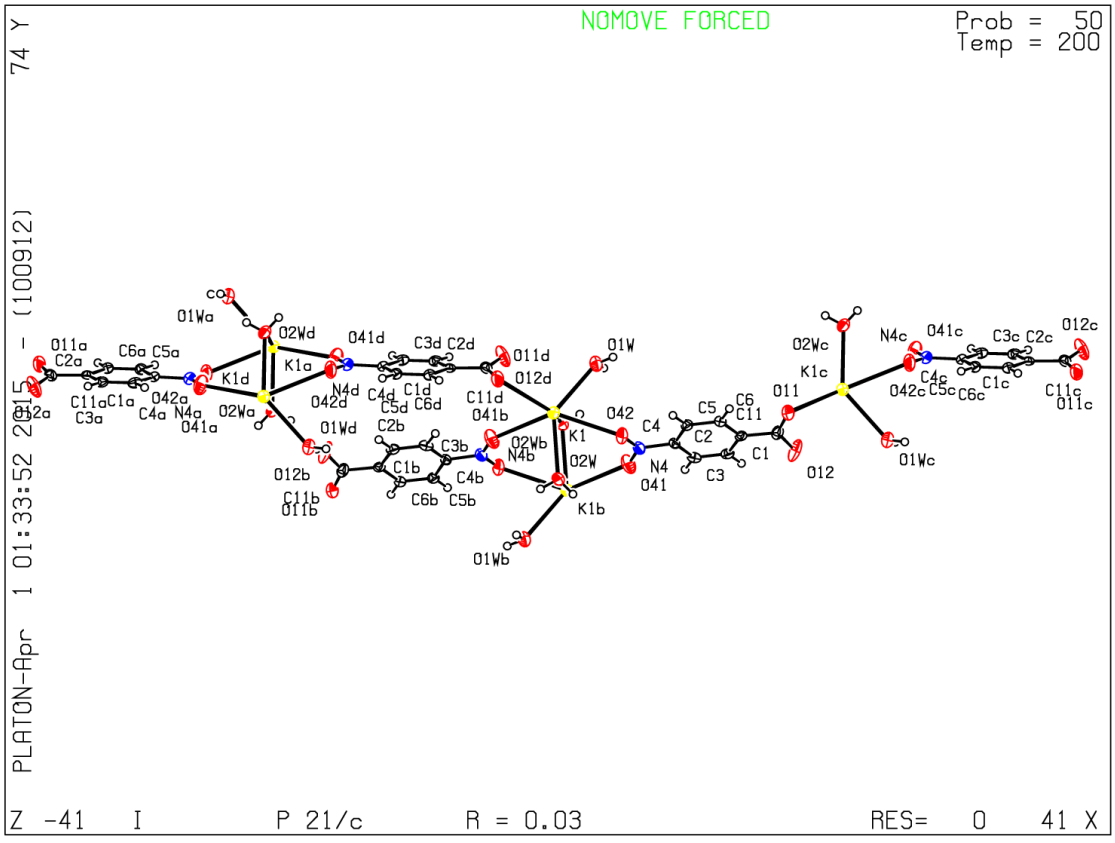
Citation comments

3 dates found in _publ_section_comment that could be part of a citation but not found in reference list: 1961, 2012, 1967

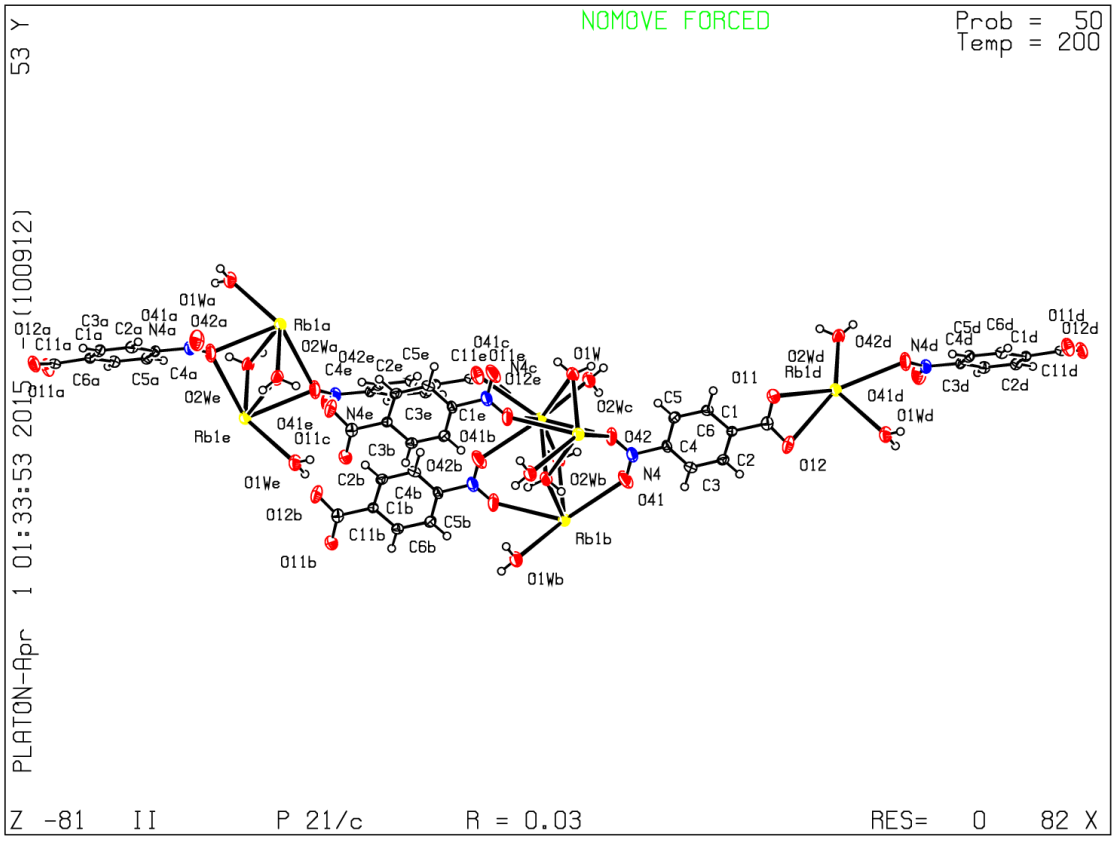
1 date found in _publ_section_figure_captions that could be part of a citation but not found in reference list: 1961

1 date found in _computing_molecular_graphics that could be part of a citation but not found in reference list: 2008

Datablock I - ellipsoid plot



Datablock II - ellipsoid plot



supporting information

The structures of the isomorphous potassiun and rubidium salts of 4-nitro-benzoic acid and an overview of the features the metal complex stereochemistries of the alkali metal salt series with this ligand

Graham Smith

Computing details

For both compounds, data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) for (I); *SIR92* (Altomare *et al.*, 1993) for (II). For both compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012). Molecular graphics: *PLATON* (Spek, 2009) for (I); *PLATON* (Spek, 2008) for (II). For both compounds, software used to prepare material for publication: *PLATON*.

(I)

Crystal data

$C_7H_8KNO_6$
M_r = 241.24
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 5.8217 (4) Å
b = 6.9692 (5) Å
c = 23.8602 (16) Å
β = 97.299 (6)°
V = 960.23 (12) Å^3
Z = 4
$F(000)$ = 496
D_x = 1.669 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1787 reflections
θ = 3.6–28.4°
μ = 0.56 mm^{-1}
T = 200 K
Plate, colourless
0.30 × 0.25 × 0.08 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.077 pixels mm^{-1}
ω scans
Absorption correction: multi-scan *CrysAlis PRO* (Agilent, 2013)
T_{min} = 0.945, T_{max} = 0.980
3638 measured reflections
1886 independent reflections
1755 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 26.0°, θ_{min} = 3.4°
h = −6→7
k = −5→8
l = −25→29

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.073
S = 1.04
1886 reflections
136 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.1983P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
K1	0.77670 (6)	0.69041 (6)	1.02388 (1)	0.0276 (1)
O1W	0.7292 (2)	0.9884 (2)	0.94571 (5)	0.0356 (4)
O2W	0.7330 (2)	0.30012 (19)	1.01672 (5)	0.0370 (4)
O11	1.0168 (3)	0.6385 (2)	0.63127 (5)	0.0437 (5)
O12	0.7106 (2)	0.4571 (3)	0.60516 (6)	0.0514 (5)
O41	0.4839 (3)	0.4220 (3)	0.88176 (6)	0.0512 (5)
O42	0.8214 (3)	0.5415 (2)	0.90923 (6)	0.0452 (5)
N4	0.6699 (3)	0.4893 (2)	0.87230 (6)	0.0311 (5)
C1	0.7928 (3)	0.5361 (2)	0.70211 (7)	0.0209 (5)
C2	0.5842 (3)	0.4621 (2)	0.71540 (7)	0.0247 (5)
C3	0.5418 (3)	0.4481 (2)	0.77096 (8)	0.0248 (5)
C4	0.7122 (3)	0.5086 (2)	0.81307 (7)	0.0227 (5)
C5	0.9195 (3)	0.5860 (2)	0.80152 (7)	0.0233 (5)
C6	0.9576 (3)	0.6003 (2)	0.74560 (7)	0.0218 (5)
C11	0.8449 (3)	0.5455 (3)	0.64141 (7)	0.0292 (5)
H2	0.46970	0.42070	0.68590	0.0300*
H3	0.39930	0.39810	0.78000	0.0300*
H5	1.03270	0.62830	0.83110	0.0280*
H6	1.09820	0.65460	0.73670	0.0260*
H11W	0.59450	0.98250	0.92560	0.0530*
H12W	0.81490	1.01440	0.92060	0.0530*
H21W	0.74160	0.24130	1.04820	0.0550*
H22W	0.72240	0.21050	0.99140	0.0550*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0331 (2)	0.0256 (2)	0.0239 (2)	0.0001 (2)	0.0034 (2)	−0.0004 (2)
O1W	0.0388 (7)	0.0417 (8)	0.0262 (7)	−0.0009 (6)	0.0043 (5)	0.0039 (6)
O2W	0.0593 (8)	0.0268 (7)	0.0238 (6)	−0.0026 (7)	0.0011 (6)	0.0046 (6)
O11	0.0629 (9)	0.0411 (9)	0.0311 (8)	−0.0084 (8)	0.0212 (7)	−0.0019 (6)
O12	0.0420 (8)	0.0806 (12)	0.0294 (8)	0.0082 (8)	−0.0037 (6)	−0.0264 (8)
O41	0.0514 (9)	0.0649 (11)	0.0418 (8)	−0.0068 (8)	0.0231 (7)	0.0122 (8)

O42	0.0664 (9)	0.0480 (9)	0.0211 (7)	−0.0090 (8)	0.0055 (6)	−0.0036 (6)
N4	0.0429 (9)	0.0255 (8)	0.0265 (8)	0.0026 (7)	0.0111 (7)	0.0042 (7)
C1	0.0253 (8)	0.0139 (8)	0.0228 (8)	0.0052 (7)	0.0006 (6)	−0.0004 (6)
C2	0.0268 (8)	0.0183 (8)	0.0269 (9)	−0.0007 (7)	−0.0051 (7)	−0.0009 (7)
C3	0.0208 (8)	0.0185 (8)	0.0352 (10)	−0.0009 (7)	0.0043 (6)	0.0034 (7)
C4	0.0309 (8)	0.0173 (8)	0.0205 (8)	0.0031 (7)	0.0060 (7)	0.0034 (7)
C5	0.0268 (8)	0.0199 (8)	0.0220 (8)	−0.0008 (7)	−0.0014 (6)	−0.0003 (7)
C6	0.0223 (8)	0.0194 (8)	0.0237 (9)	−0.0010 (7)	0.0028 (6)	0.0009 (7)
C11	0.0366 (9)	0.0275 (10)	0.0228 (9)	0.0126 (9)	0.0010 (7)	−0.0023 (8)

Geometric parameters (Å, º)

K1—O1W	2.7816 (14)	O2W—H22W	0.8700
K1—O2W	2.7352 (14)	N4—C4	1.471 (2)
K1—O42	2.9681 (15)	C1—C2	1.393 (2)
K1—O2W^{i}	3.0029 (12)	C1—C6	1.394 (2)
K1—O41^{i}	2.9752 (17)	C1—C11	1.518 (2)
K1—O11^{ii}	3.0051 (14)	C2—C3	1.382 (3)
O11—C11	1.242 (2)	C3—C4	1.385 (2)
O12—C11	1.252 (2)	C4—C5	1.381 (2)
O41—N4	1.227 (2)	C5—C6	1.384 (2)
O42—N4	1.220 (2)	C2—H2	0.9500
O1W—H11W	0.8700	C3—H3	0.9500
O1W—H12W	0.8500	C5—H5	0.9500
O2W—H21W	0.8500	C6—H6	0.9500
O1W—K1—O2W	134.43 (4)	K1^{i}—O2W—H22W	79.00
O1W—K1—O42	69.87 (4)	O41—N4—O42	123.70 (16)
O1W—K1—O2W^{i}	75.95 (4)	O41—N4—C4	118.10 (15)
O1W—K1—O41^{i}	133.41 (5)	O42—N4—C4	118.20 (16)
O1W—K1—O11^{ii}	105.75 (4)	C2—C1—C6	119.13 (15)
O2W—K1—O42	67.24 (4)	C2—C1—C11	121.26 (15)
O2W—K1—O2W^{i}	85.49 (4)	C6—C1—C11	119.61 (15)
O2W—K1—O41^{i}	74.52 (5)	C1—C2—C3	120.77 (16)
O2W—K1—O11^{ii}	118.51 (4)	C2—C3—C4	118.39 (16)
O2W^{i}—K1—O42	84.78 (4)	N4—C4—C5	118.98 (15)
O41^{i}—K1—O42	135.91 (5)	C3—C4—C5	122.52 (16)
O11^{ii}—K1—O42	147.02 (5)	N4—C4—C3	118.50 (15)
O2W^{i}—K1—O41^{i}	70.85 (4)	C4—C5—C6	118.14 (15)
O2W^{i}—K1—O11^{ii}	126.86 (4)	C1—C6—C5	121.00 (16)
O11^{ii}—K1—O41^{i}	71.70 (5)	O11—C11—C1	118.17 (15)
K1—O2W—K1^{i}	94.51 (4)	O12—C11—C1	117.06 (16)
K1^{iii}—O11—C11	94.25 (11)	O11—C11—O12	124.78 (16)
K1^{i}—O41—N4	141.87 (11)	C1—C2—H2	120.00
K1—O42—N4	129.04 (13)	C3—C2—H2	120.00
H11W—O1W—H12W	101.00	C2—C3—H3	121.00
K1—O1W—H11W	110.00	C4—C3—H3	121.00
K1—O1W—H12W	128.00	C4—C5—H5	121.00

K1^{i}—O2W—H21W	104.00	C6—C5—H5	121.00
K1—O2W—H21W	115.00	C1—C6—H6	119.00
K1—O2W—H22W	139.00	C5—C6—H6	120.00
H21W—O2W—H22W	105.00		
O1W—K1—O2W—K1^{i}	−65.28 (6)	K1^{i}—O41—N4—C4	177.52 (15)
O42—K1—O2W—K1^{i}	−86.23 (5)	K1—O42—N4—O41	−28.5 (2)
O2W^{i}—K1—O2W—K1^{i}	0.00 (5)	K1—O42—N4—C4	151.36 (11)
O41^{i}—K1—O2W—K1^{i}	71.36 (4)	O41—N4—C4—C3	−0.7 (2)
O11^{ii}—K1—O2W—K1^{i}	129.94 (4)	O41—N4—C4—C5	179.30 (17)
O1W—K1—O42—N4	−86.38 (14)	O42—N4—C4—C3	179.45 (15)
O2W—K1—O42—N4	77.84 (14)	O42—N4—C4—C5	−0.5 (2)
O2W^{i}—K1—O42—N4	−9.45 (14)	C6—C1—C2—C3	−1.4 (2)
O41^{i}—K1—O42—N4	45.96 (16)	C11—C1—C2—C3	177.75 (15)
O11^{ii}—K1—O42—N4	−174.44 (12)	C2—C1—C6—C5	2.0 (2)
O1W—K1—O2W^{i}—K1^{i}	138.03 (4)	C11—C1—C6—C5	−177.18 (15)
O2W—K1—O2W^{i}—K1^{i}	0.00 (4)	C2—C1—C11—O11	169.32 (16)
O42—K1—O2W^{i}—K1^{i}	67.51 (4)	C2—C1—C11—O12	−11.1 (3)
O1W—K1—O41^{i}—N4^{i}	70.9 (3)	C6—C1—C11—O11	−11.5 (3)
O2W—K1—O41^{i}—N4^{i}	−66.6 (2)	C6—C1—C11—O12	168.09 (17)
O42—K1—O41^{i}—N4^{i}	−36.3 (3)	C1—C2—C3—C4	−0.3 (2)
O1W—K1—O11^{ii}—C11^{ii}	72.22 (12)	C2—C3—C4—N4	−178.47 (13)
O2W—K1—O11^{ii}—C11^{ii}	−119.01 (11)	C2—C3—C4—C5	1.5 (2)
O42—K1—O11^{ii}—C11^{ii}	149.37 (11)	N4—C4—C5—C6	179.03 (13)
K1^{iii}—O11—C11—O12	41.0 (2)	C3—C4—C5—C6	−1.0 (2)
K1^{iii}—O11—C11—C1	−139.42 (15)	C4—C5—C6—C1	−0.8 (2)
K1^{i}—O41—N4—O42	−2.7 (3)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) *x*, −*y*+3/2, *z*+1/2; (iii) *x*, −*y*+3/2, *z*−1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···O12^{iv}	0.87	1.84	2.6994 (17)	170
O1*W*—H12*W*···O11^{v}	0.85	1.88	2.7101 (19)	165
O2*W*—H21*W*···O12^{vi}	0.85	1.96	2.785 (2)	162
O2*W*—H22*W*···O1*W*^{vii}	0.87	1.90	2.7534 (18)	170

Symmetry codes: (iv) −*x*+1, *y*+1/2, −*z*+3/2; (v) −*x*+2, *y*+1/2, −*z*+3/2; (vi) *x*, −*y*+1/2, *z*+1/2; (vii) *x*, *y*−1, *z*.

(II)

Crystal data

$C_7H_8NO_6Rb$	V = 1000.44 (16) Å^3
M_r = 287.61	Z = 4
Monoclinic, $P2_1/c$	F(000) = 568
Hall symbol: -P 2ybc	D_x = 1.910 Mg m^{-3}
a = 5.9355 (5) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 7.0456 (7) Å	Cell parameters from 1174 reflections
c = 24.204 (2) Å	θ = 3.5–28.5°
β = 98.739 (8)°	μ = 4.96 mm^{-1}

T = 200 K
Plate, colourless

0.31 × 0.24 × 0.10 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.077 pixels mm^{-1}
ω scans
Absorption correction: multi-scan *CrysAlis PRO* (Agilent, 2013)
T_{min} = 0.549, T_{max} = 0.980

3439 measured reflections
1969 independent reflections
1692 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 26.0°, θ_{min} = 3.4°
$h = -7 \rightarrow 4$
$k = -7 \rightarrow 8$
$l = -28 \rightarrow 29$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.082
S = 0.97
1969 reflections
137 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}
Extinction correction: *SHELXL97*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0184 (13)

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Rb1	0.78049 (5)	0.69598 (4)	1.02561 (1)	0.0255 (1)
O1W	0.7211 (4)	0.9980 (4)	0.94096 (11)	0.0354 (8)
O2W	0.7393 (4)	0.2888 (3)	1.01744 (11)	0.0337 (8)
O11	1.0358 (4)	0.6237 (4)	0.63766 (11)	0.0383 (9)
O12	0.7228 (4)	0.4612 (4)	0.60615 (10)	0.0374 (9)
O41	0.4706 (5)	0.4209 (5)	0.87570 (12)	0.0519 (10)
O42	0.8054 (5)	0.5305 (4)	0.90717 (11)	0.0437 (10)
N4	0.6575 (5)	0.4828 (4)	0.86862 (13)	0.0310 (10)
C1	0.7987 (5)	0.5306 (4)	0.70310 (13)	0.0186 (9)
C2	0.5929 (5)	0.4550 (5)	0.71350 (14)	0.0231 (10)
C3	0.5446 (5)	0.4405 (4)	0.76745 (15)	0.0235 (10)
C4	0.7062 (5)	0.5016 (4)	0.81099 (13)	0.0212 (10)
C5	0.9124 (5)	0.5805 (5)	0.80252 (14)	0.0236 (10)

C6	0.9564 (5)	0.5940 (5)	0.74803 (13)	0.0215 (9)
C11	0.8583 (6)	0.5394 (5)	0.64466 (15)	0.0244 (10)
H2	0.48390	0.41280	0.68310	0.0280*
H3	0.40340	0.38960	0.77440	0.0280*
H5	1.01980	0.62390	0.83300	0.0280*
H6	1.09650	0.64730	0.74110	0.0260*
H11W	0.57380	0.99300	0.92080	0.0530*
H12W	0.80120	1.03010	0.91800	0.0530*
H21W	0.74790	0.23000	1.04900	0.0500*
H22W	0.72870	0.19920	0.99220	0.0500*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb1	0.0287 (2)	0.0251 (2)	0.0233 (2)	−0.0002 (1)	0.0059 (1)	−0.0004 (2)
O1W	0.0353 (13)	0.0451 (16)	0.0268 (15)	−0.0013 (12)	0.0076 (11)	0.0027 (13)
O2W	0.0494 (16)	0.0275 (14)	0.0246 (14)	−0.0020 (11)	0.0069 (12)	0.0045 (11)
O11	0.0453 (15)	0.0437 (16)	0.0295 (15)	−0.0112 (13)	0.0172 (12)	−0.0049 (13)
O12	0.0357 (14)	0.0540 (17)	0.0222 (14)	0.0036 (12)	0.0032 (11)	−0.0130 (13)
O41	0.0537 (17)	0.069 (2)	0.0381 (17)	−0.0099 (16)	0.0234 (14)	0.0118 (16)
O42	0.0633 (18)	0.0499 (18)	0.0185 (14)	−0.0014 (14)	0.0081 (13)	−0.0027 (13)
N4	0.0446 (18)	0.0286 (16)	0.0216 (17)	0.0024 (14)	0.0110 (14)	0.0030 (14)
C1	0.0243 (16)	0.0133 (15)	0.0179 (17)	−0.0003 (13)	0.0026 (13)	−0.0002 (13)
C2	0.0280 (17)	0.0173 (16)	0.0226 (18)	−0.0031 (14)	−0.0004 (14)	0.0004 (14)
C3	0.0227 (16)	0.0205 (16)	0.0282 (19)	−0.0022 (14)	0.0071 (13)	0.0032 (16)
C4	0.0298 (17)	0.0181 (16)	0.0163 (17)	0.0023 (13)	0.0058 (14)	0.0031 (14)
C5	0.0274 (17)	0.0204 (17)	0.0216 (18)	−0.0012 (14)	−0.0006 (13)	−0.0008 (15)
C6	0.0197 (15)	0.0209 (16)	0.0241 (18)	−0.0014 (13)	0.0042 (13)	−0.0009 (15)
C11	0.0279 (18)	0.0214 (17)	0.0245 (19)	0.0083 (15)	0.0059 (14)	−0.0013 (15)

Geometric parameters (Å, º)

Rb1—O1W	2.938 (3)	O2W—H21W	0.8600
Rb1—O2W	2.884 (2)	O2W—H22W	0.8700
Rb1—O42	3.119 (3)	N4—C4	1.473 (4)
Rb1—O2W^{i}	3.105 (2)	C1—C2	1.390 (4)
Rb1—O41^{i}	3.112 (3)	C1—C6	1.396 (4)
Rb1—O2W^{ii}	3.182 (2)	C1—C11	1.511 (5)
Rb1—O42^{ii}	3.165 (3)	C2—C3	1.383 (5)
Rb1—O11^{iii}	3.165 (3)	C3—C4	1.382 (5)
Rb1—O12^{iii}	3.155 (3)	C4—C5	1.388 (4)
O11—C11	1.243 (4)	C5—C6	1.386 (5)
O12—C11	1.262 (4)	C2—H2	0.9500
O41—N4	1.228 (4)	C3—H3	0.9500
O42—N4	1.227 (4)	C5—H5	0.9500
O1W—H11W	0.9300	C6—H6	0.9500
O1W—H12W	0.8200		

O1W—Rb1—O2W	132.29 (8)		Rb1^{iv}—O12—C11	90.3 (2)
O1W—Rb1—O42	69.34 (7)		Rb1^{i}—O41—N4	138.5 (2)
O1W—Rb1—O2W^{i}	74.52 (7)		Rb1—O42—N4	132.3 (2)
O1W—Rb1—O41^{i}	134.93 (8)		Rb1—O42—Rb1^{ii}	81.81 (6)
O1W—Rb1—O2W^{ii}	76.45 (6)		Rb1^{ii}—O42—N4	131.5 (2)
O1W—Rb1—O42^{ii}	136.48 (7)		H11W—O1W—H12W	104.00
O1W—Rb1—O11^{iii}	107.34 (7)		Rb1—O1W—H11W	110.00
O1W—Rb1—O12^{iii}	82.16 (7)		Rb1—O1W—H12W	131.00
O2W—Rb1—O42	65.19 (7)		Rb1^{i}—O2W—H21W	104.00
O2W—Rb1—O2W^{i}	86.66 (6)		Rb1—O2W—H21W	115.00
O2W—Rb1—O41^{i}	75.16 (8)		Rb1—O2W—H22W	140.00
O2W—Rb1—O2W^{ii}	94.70 (6)		H21W—O2W—H22W	105.00
O2W—Rb1—O42^{ii}	65.47 (7)		Rb1^{ii}—O2W—H22W	77.00
O2W—Rb1—O11^{iii}	118.86 (7)		Rb1^{ii}—O2W—H21W	112.00
O2W—Rb1—O12^{iii}	142.00 (7)		Rb1^{i}—O2W—H22W	80.00
O2W^{i}—Rb1—O42	83.56 (7)		O41—N4—O42	123.3 (3)
O41^{i}—Rb1—O42	134.56 (8)		O42—N4—C4	118.4 (3)
O2W^{ii}—Rb1—O42	62.72 (7)		O41—N4—C4	118.4 (3)
O42—Rb1—O42^{ii}	98.19 (7)		C2—C1—C11	121.5 (3)
O11^{iii}—Rb1—O42	148.68 (7)		C2—C1—C6	119.0 (3)
O12^{iii}—Rb1—O42	151.50 (7)		C6—C1—C11	119.5 (3)
O2W^{i}—Rb1—O41^{i}	72.51 (7)		C1—C2—C3	120.9 (3)
O2W^{i}—Rb1—O2W^{ii}	141.53 (7)		C2—C3—C4	118.6 (3)
O2W^{i}—Rb1—O42^{ii}	147.60 (7)		C3—C4—C5	122.5 (3)
O2W^{i}—Rb1—O11^{iii}	126.57 (7)		N4—C4—C3	118.8 (3)
O2W^{i}—Rb1—O12^{iii}	89.16 (6)		N4—C4—C5	118.7 (3)
O2W^{ii}—Rb1—O41^{i}	144.83 (7)		C4—C5—C6	117.8 (3)
O41^{i}—Rb1—O42^{ii}	84.10 (8)		C1—C6—C5	121.2 (3)
O11^{iii}—Rb1—O41^{i}	70.81 (7)		O11—C11—O12	124.5 (3)
O12^{iii}—Rb1—O41^{i}	67.59 (8)		O11—C11—C1	118.1 (3)
O2W^{ii}—Rb1—O42^{ii}	61.38 (7)		O12—C11—C1	117.4 (3)
O2W^{ii}—Rb1—O11^{iii}	86.04 (6)		C1—C2—H2	120.00
O2W^{ii}—Rb1—O12^{iii}	111.30 (6)		C3—C2—H2	120.00
O11^{iii}—Rb1—O42^{ii}	61.88 (7)		C2—C3—H3	121.00
O12^{iii}—Rb1—O42^{ii}	102.54 (7)		C4—C3—H3	121.00
O11^{iii}—Rb1—O12^{iii}	41.06 (7)		C4—C5—H5	121.00
Rb1—O2W—Rb1^{i}	93.34 (6)		C6—C5—H5	121.00
Rb1—O2W—Rb1^{ii}	85.30 (6)		C1—C6—H6	119.00
Rb1^{i}—O2W—Rb1^{ii}	141.53 (9)		C5—C6—H6	119.00
Rb1^{iv}—O11—C11	90.2 (2)			

O1W—Rb1—O2W—Rb1^{i}	−65.51 (10)	O1W—Rb1—O42^{ii}—Rb1^{ii}	−68.52 (11)
O1W—Rb1—O2W—Rb1^{ii}	75.94 (9)	O1W—Rb1—O42^{ii}—N4^{ii}	72.8 (3)
O42—Rb1—O2W—Rb1^{i}	−84.45 (8)	O2W—Rb1—O42^{ii}—Rb1^{ii}	57.88 (7)
O42—Rb1—O2W—Rb1^{ii}	57.00 (7)	O2W—Rb1—O42^{ii}—N4^{ii}	−160.8 (3)
O2W^{i}—Rb1—O2W—Rb1^{i}	0.00 (8)	O42—Rb1—O42^{ii}—Rb1^{ii}	0.00 (8)
O2W^{i}—Rb1—O2W—Rb1^{ii}	141.45 (7)	O42—Rb1—O42^{ii}—N4^{ii}	141.3 (3)
O41^{i}—Rb1—O2W—Rb1^{i}	72.78 (7)	O1W—Rb1—O11^{iii}—C11^{iii}	73.8 (2)

O41^{i}—Rb1—O2W—Rb1^{ii}	−145.77 (8)	O2W—Rb1—O11^{iii}—C11^{iii}	−118.5 (2)
O2W^{ii}—Rb1—O2W—Rb1^{i}	−141.45 (7)	O42—Rb1—O11^{iii}—C11^{iii}	152.4 (2)
O2W^{ii}—Rb1—O2W—Rb1^{ii}	0.00 (7)	O1W—Rb1—O12^{iii}—C11^{iii}	−146.7 (2)
O42^{ii}—Rb1—O2W—Rb1^{i}	163.01 (9)	O2W—Rb1—O12^{iii}—C11^{iii}	55.3 (2)
O42^{ii}—Rb1—O2W—Rb1^{ii}	−55.54 (7)	O42—Rb1—O12^{iii}—C11^{iii}	−146.4 (2)
O11^{iii}—Rb1—O2W—Rb1^{i}	130.49 (7)	Rb1^{iv}—O11—C11—O12	40.4 (4)
O11^{iii}—Rb1—O2W—Rb1^{ii}	−88.06 (7)	Rb1^{iv}—O11—C11—C1	−139.2 (3)
O12^{iii}—Rb1—O2W—Rb1^{i}	84.35 (11)	Rb1^{iv}—O12—C11—O11	−40.5 (4)
O12^{iii}—Rb1—O2W—Rb1^{ii}	−134.21 (9)	Rb1^{iv}—O12—C11—C1	139.0 (3)
O1W—Rb1—O42—N4	−82.5 (3)	Rb1^{i}—O41—N4—O42	−5.7 (6)
O1W—Rb1—O42—Rb1^{ii}	136.78 (8)	Rb1^{i}—O41—N4—C4	174.6 (2)
O2W—Rb1—O42—N4	82.7 (3)	Rb1—O42—N4—O41	−30.2 (5)
O2W—Rb1—O42—Rb1^{ii}	−58.09 (7)	Rb1—O42—N4—C4	149.5 (2)
O2W^{i}—Rb1—O42—N4	−6.6 (3)	Rb1^{ii}—O42—N4—O41	93.0 (4)
O2W^{i}—Rb1—O42—Rb1^{ii}	−147.38 (7)	Rb1^{ii}—O42—N4—C4	−87.3 (3)
O41^{i}—Rb1—O42—N4	51.0 (3)	O41—N4—C4—C3	−3.1 (4)
O41^{i}—Rb1—O42—Rb1^{ii}	−89.76 (11)	O41—N4—C4—C5	176.7 (3)
O2W^{ii}—Rb1—O42—N4	−167.5 (3)	O42—N4—C4—C3	177.2 (3)
O2W^{ii}—Rb1—O42—Rb1^{ii}	51.78 (6)	O42—N4—C4—C5	−3.0 (4)
O42^{ii}—Rb1—O42—N4	140.8 (3)	C6—C1—C2—C3	−0.7 (5)
O42^{ii}—Rb1—O42—Rb1^{ii}	0.00 (8)	C11—C1—C2—C3	177.3 (3)
O11^{iii}—Rb1—O42—N4	−172.1 (2)	C2—C1—C6—C5	0.9 (5)
O11^{iii}—Rb1—O42—Rb1^{ii}	47.18 (15)	C11—C1—C6—C5	−177.1 (3)
O12^{iii}—Rb1—O42—N4	−82.8 (3)	C2—C1—C11—O11	173.8 (3)
O12^{iii}—Rb1—O42—Rb1^{ii}	136.44 (12)	C2—C1—C11—O12	−5.8 (5)
O1W—Rb1—O2W^{i}—Rb1^{i}	135.69 (9)	C6—C1—C11—O11	−8.3 (5)
O2W—Rb1—O2W^{i}—Rb1^{i}	0.00 (7)	C6—C1—C11—O12	172.1 (3)
O42—Rb1—O2W^{i}—Rb1^{i}	65.39 (7)	C1—C2—C3—C4	−0.5 (5)
O1W—Rb1—O41^{i}—N4^{i}	66.1 (4)	C2—C3—C4—N4	−178.8 (3)
O2W—Rb1—O41^{i}—N4^{i}	−69.8 (4)	C2—C3—C4—C5	1.4 (5)
O42—Rb1—O41^{i}—N4^{i}	−40.3 (4)	N4—C4—C5—C6	179.0 (3)
O1W—Rb1—O2W^{ii}—Rb1^{ii}	−132.43 (8)	C3—C4—C5—C6	−1.2 (5)
O2W—Rb1—O2W^{ii}—Rb1^{ii}	0.00 (7)	C4—C5—C6—C1	0.1 (5)
O42—Rb1—O2W^{ii}—Rb1^{ii}	−58.93 (7)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) −*x*+2, −*y*+1, −*z*+2; (iii) *x*, −*y*+3/2, *z*+1/2; (iv) *x*, −*y*+3/2, *z*−1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···O12^{v}	0.93	1.80	2.720 (3)	169
O1*W*—H12*W*···O11^{vi}	0.82	1.89	2.706 (4)	174
O2*W*—H21*W*···O12^{vii}	0.86	1.95	2.790 (4)	163
O2*W*—H22*W*···O1*W*^{viii}	0.87	1.88	2.752 (4)	176

Symmetry codes: (v) −*x*+1, *y*+1/2, −*z*+3/2; (vi) −*x*+2, *y*+1/2, −*z*+3/2; (vii) *x*, −*y*+1/2, *z*+1/2; (viii) *x*, *y*−1, *z*.